AL-TR-90-019

AD:

AD-A224 343

Final Report
for the period
August 1986 to
July 1989

Experimental Studies Leading to Energy Storage

Spectroscopy and Dynamics of Polyatomic Hydrogen in Liquid, Solid and Gaseous Hydrogen Plasmas

June 1990

Author:
T. Oka

University of Chicago
Department of Chemistry
5735 S. Ellis Street
Chicago IL 60637

F04611-86-K-0069

Approved for Public Release

Prepared for the: **Astronautics Laboratory (AFSC)**
Air Force Space Technology Center
Space Systems Division
Air Force Systems Command
Edwards AFB CA 93523-5000

NOTICE

When U.S. Government drawings, specifications, or other data are used for any purpose other than a definitely related Government procurement operation, the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise, or in any way licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may be related thereto.

FOREWORD

This final report was submitted by University of Chicago, Chicago IL on completion of contract F04611-86-K-0069 with the Astronautics Laboratory (AFSC), Edwards Air Force Base, CA. AL Project Manager was Capt Tim Wiley.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the DD Form 1473.

TIMOTHY G. WILEY, CAPT, USAF
Project Manager

STEPHEN L. RODGERS
Chief, Advanced Research in Energy Storage Office

FOR THE DIRECTOR

ROBERT C. CORLEY
Director, Astronautical Sciences Division

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION: UNCLASSIFIED	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for Public Release; Distribution is Unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S): AL-TR-90-019
6a. NAME OF PERFORMING ORGANIZATION: University of Chicago; 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION: Astronautics Laboratory (AFSC)
6c. ADDRESS (City, State, and ZIP Code): Department of Chemistry, 5735 S. Ellis Avenue, Chicago, IL 60637	7b. ADDRESS (City, State, and ZIP Code): AL/LSX, Edwards AFB CA 93523-5000
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: Department of the Air Force; 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: F04611-86-K-0069
8c. ADDRESS (City, State, and ZIP Code): Astronautics Laboratory, Edwards Air Force Base, CA 93523-5000	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. / PROJECT NO. 5730 / TASK NO 00QV / WORK UNIT ACCESSION NO. DF 342430

11. TITLE (Include Security Classification)
EXPERIMENTAL STUDIES LEADING TO ENERGY STORAGE. Spectroscopy and Dynamics of Polyatomic Hydrogen in Liquid, Solid and Gaseous Hydrogen Plasmas (U)

12. PERSONAL AUTHOR(S)
Oka, Takeshi

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final Summary	FROM 8/86 TO 7/89	90/06	29

16. SUPPLEMENTARY NOTATION

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP
07	04	
21	09	

18. SUBJECT TERMS (~~Continue on reverse if necessary and identify by block number~~)
Polyatomic hydrogen, Solid hydrogen, Plasmas, H_3^+, Laser infrared spectroscopy, Dynamics

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

During the three years of this contract the research has been conducted in the following four areas and led to significant developments.

1) We have observed infrared spectrum of ionized solid hydrogen produced by high energy (2 3 MeV) bombardment of electrons. The spectrum gave vibrational frequencies of H_3^+ and its hydrogen clusters in the solid. This has opened up a new method of ion spectroscopy in solids.

2) We have observed extremely sharp solid hydrogen spectral lines in nearly pure para-solid hydrogen. This was the first time that an optical spectrum was observed with such high resolution and opened a new direction in condensed phase spectroscopy and the study of intermolecular interaction.

(continued on reverse side)

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	UNCLASSIFIED

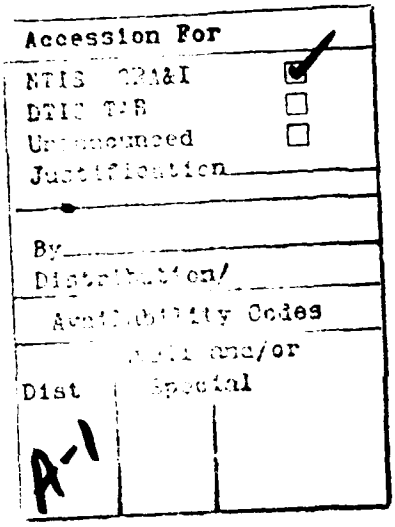
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Captain Timothy Wiley	805-277-5749	AFFTC/PKRA AL/LSX

DD Form 1473, JUN 86 — Previous editions are obsolete. — SECURITY CLASSIFICATION OF THIS PAGE

3) We have observed the H_3^+ spectrum in highly excited vibrational states. Our results have not only provided insight into the H_3^+ excitation in plasmas but also led to the definitive assignment of the Jupiter H_3^+ emission spectrum accidentally discovered by astronomets.

4) We have observed the H_3^+ fundamental emission band in Jupiter which revealed interesting and intricate dynamical behavior of Jupiter plasmas.

All these developments far exceeded my anticipation at the time of writing the proposal four years ago.



CONTENT

Introduction

A chronological summary of events related to this proposal is given in Table 1. It is truly amazing how quickly these three years have passed. I feel as if it was yesterday that I started ordering the apparatus. While these three years passed so quickly, they were extremely rich years, as we can see from Table 1. I did not anticipate at the writing of the proposal that such a rich research period had awaited us. When I read my original proposal written in March-April 1986, I realize that by and large I overestimated the experimental difficulties. I was a little too cautious to go into the fields of low temperature and condensed phase spectroscopy both of which had been entirely new to me. Things have been easier than I thought!

There have been two experiments in my proposal that were tried but did not work well. The first was the spectroscopy of liquid hydrogen. We did the experiment but found that liquid does not give interesting results. The spectral lines are broad and could not be analyzed in any more detail than had already been done. The ions generated in liquid are lost very quickly due to electron recombination. I do not think much can be done to remedy these situations and I shall not pursue this line of research further. The second failure was the search for the spectrum of gaseous H_5^+ in hydrogen plasmas. We attempted this twice for H_5^+ and once for D_5^+ but could not find any spectral line in the expected wavelength regions. I believe we were not doing chemistry right and plan to come back to it using different plasmas. Next time we will try hollow cathode discharges instread of positive column discharges. These experiments will not be discussed further in this report.

Many parts of our project went more or less according to our expectations. Many new spectral features were observed when solid hydrogen samples were ionized by accelerated electron beams with the energy of ~2 MeV. The observed features are tentatively assigned to various vibrational modes of H_3^+ and its hydrogenated clusters but more experimental and theoretical effort will be needed to obtain more definitive information. This part of the experiment will be discussed in the section on Spectroscopy of Ionized Solid Hydrogen. Our observation of vibrationally excited H_3^+ has been extremely productive. The observed spectrum was very difficult to analyze and we were lucky to have had the very timely theoretical help of Steve Miller and Jonathan Tennyson. Because of their help our observed spectrum has been very thoroughly analyzed. This part of the experiment, which includes the construction of a new difference frequency laser system, will be discussed later.

The most exciting results came from two developments, both of which were totally unexpected at the time of writing the proposal. We observed extremely sharp and rich spectral lines in solid hydrogen. Contrary to the conventional notion that optical spectra of solids are broad, due to strong intermolecular interaction, we found very sharp lines indicating a very discrete quantum state with long relaxation time. Under certain conditions the solid state spectral lines are sharper than gaseous lines! I believe we have found a new direction in high resolution spectroscopy. The second unexpected excitement came from planet Jupiter. In September of last year, astronomers in Canada-French-Hawaii-Telescope observed a set of strong infrared emission lines which could not be assigned to any known molecules. Based on our laboratory spectrum the spectral lines have been assigned to the overtone emission band

$2\nu_2 \rightarrow O$ of H_3^+. Subequently I used the United Kingdom Infrared Telescope to observe the fundamental emission band $\nu_2 \rightarrow O$ in the auroral regions of Jupiter. This development will be described later.

Table 1

Chronological Summary of Events

February 1986	Air Force HEDM notice
March-April	Proposal drafted
May 2	Proposal sent
August	Budget granted. Purchasing started
September	Graduate student Man-Chor Chan joined the group
September-December	Absorption cell and vacuum system designed and constructed.
January 1987	Postdoctorate fellow Mitchio Okumura joined the group
February	Inova-100 Ar ion laser arrived
February 2	Steve Rodgers and Walter Lauderdale visited
February-May	Preparation of transparent H_2 crystal was successful
	Hollow cathode discharge cell constructed.
May 12-13	Attended HEDM meeting
May 19-21	Man-Chor Chan attended an FTIR machine course given by BOMEM
June 7	BOMEM DA-2 Fourier Transform Spectrometer
June 29	Luc Rochet from BOMEM assembled the spectrometer
August	Spectral search for D_5^+
September 17-18	Luc Rochet adjusted the spectrometer
October	$LiIO_3$ mixer completed
December	Solid spectrum of H_2 obtained using DA-2

January 1988	H_3^+ hot band $2\nu_2$ (= 2) ← ν_2 observed and assigned
February 28-March 2	HEDM meeting
March-May	H_3^+ hot bands $2\nu_2$ (= O) ← ν_2 and $\nu_1 + \nu_2$ ← ν_1 observed
and	assigned
June	The tetrahexacontapole spectrum of H_2 observed
July	Multiphoton ionizatioin using an excimer laser attempted. Extremely rich $Q_1(1)$ band spectrum of H_2 observed.
July 25	Monte Turner visited
July 27,28, Aug. 12,15	Accelerator experiments at Argonne National Lab.
September-December	Solid H_2 impurity experiments CH_4, CO, D_2
January 1989	Accelerator experiments
February 3	New proposal submitted
March 12-15	HEDM meeting
May 10,11,12	Accelerator experiments
May-June	H_3^+ overtone band $2\nu_2$ ← O observed and analyzed
July-August	Theoretical study of solid H_2
September	H_3^+ fundamental emission band observed in Jupiter

---

Spectroscopy of Ionized Solid Hydrogen

The Idea

The idea for this experiment was conceived when I thought of producing polyatomic hydrogenic species in the solid phase and observing them by their infrared spectra. A solid hydrogen crystal is bombarded with a beam of accelerated electrons with the energy of a few MeV. The sequence of events producing polyatomic hydrogenic ions occurs as shown in Fig. 1.

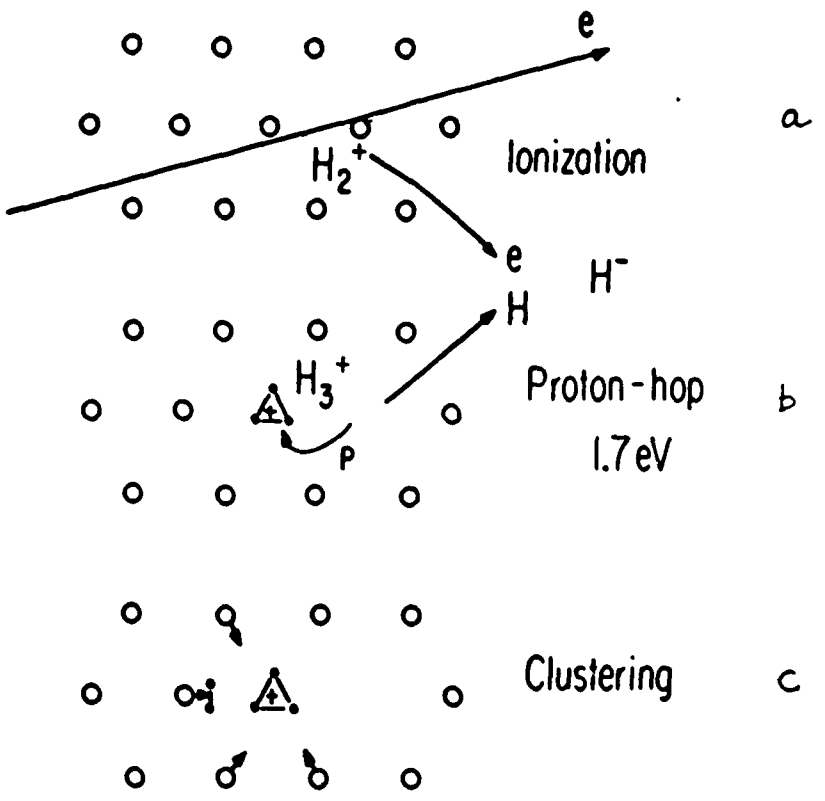


Figure 1. The sequence of events in electron bombarded solid hydrogen.

In Fig. 1a, many H_2 molecules are ionized by energetic electrons. Many of the ejected secondary electrons have sufficient energies to fly apart from the remaining H_2^+ and do not recombine quickly. In Fig. 1b, a proton hops from H_2^+ to a nearest neighbor H_2 to produce H_3^+. The larger proton affinity of H_2 (4.4 eV) than that of H (2.7 eV) makes this reaction highly exothermic (1.7 eV) and the proximity of the nearest neighbor molecules (3.8 Å) makes the reaction instantaneous. The exothermicity is absorbed

partly as the internal energy of the newly produced H_3^+, partly by the remaining H and partly by the surrounding hydrogen molecules. The energy absorbed by H_3^+ will be eventually dissipate into surrounding molecules. The excess energy imparted to H makes it fly apart from the site. The free electron and hyrogen atom ejected from the site by processes (a) and (b), respectively, wander around in the crystal until they reach the wall or find each other to combine to form H^- and stabilize. The electron might recombine with other H_3^+ during this process.

In Fig. lc, the resultant H_3^+ will attract neighboring H_2 by the Langevin force to form ionic clusters such as H_5^+, H_7^+, H_9^+, . . . H_{13}^+, . . . etc.

Experiment

A schematic diagram of the experimental setup is shown in Fig. 2.

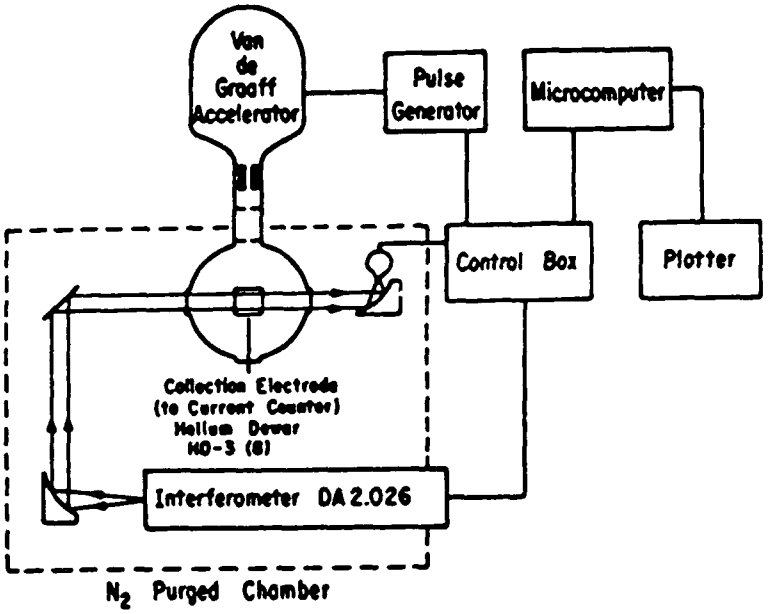


Figure 2. Block diagram of the experiment.

A transparent solid hydrogen crystal is grown in a cylindrical sample cell made of copper (~2 MeV) from a van de Graaff accelerator (we used the one in the Argonne National Laboratory). The beam enters the cell through a Ni foil (thickness which is sealed with an In O-ring. Electronic crystals are collected and the current measured. The infrared radiation for spectroscopy enters the cell and exit through two sapphire windows which are sealed with In O-rings. A Bomem DA-2 FTIR spectrometer is used for spectroscopy and data accumulation. The sampling of the infrared is synchronized with the pulsing of the van de Graaff acceleration to maximize the efficiency of data collection in case the lifetime of produced ions is short.

The experiments were conducted on the following nine days: July 26, 27, 1988, August 12, 15, 1988, September 29, 30, 1988, May 10, 11, 12, 1989.

Observed Spectrum

Examples of observed spectra are shown in Fig. 3. The new spectral lines induced by the electron beam bombardments are indicated with arrows. Observed frequencies and their tentative assignments are summarized in Table 2.

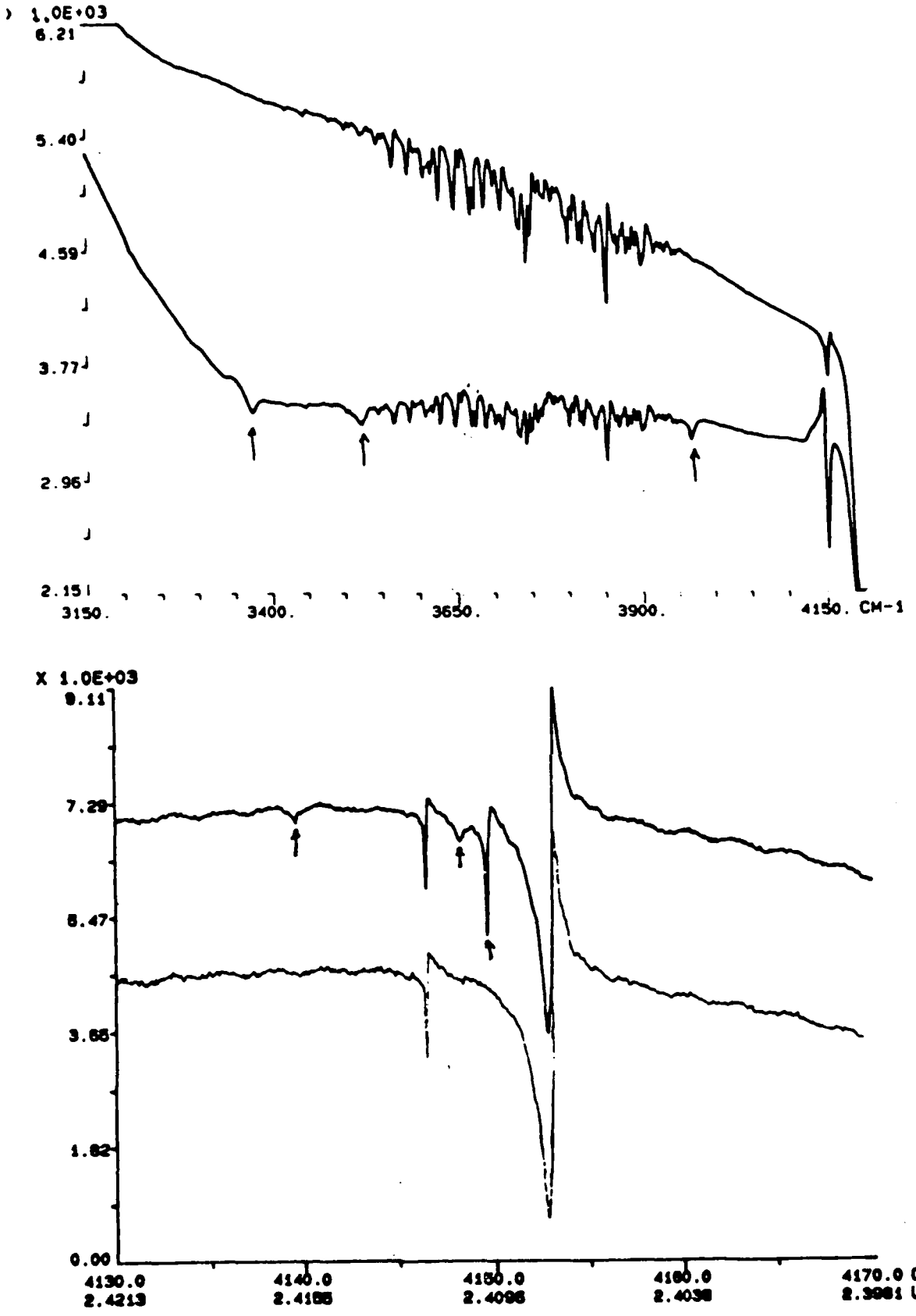


Figure 3. Solid p-H_2 spectrum without ionization (upper trace) and with ionization (lower trace). The three new features are marked with arrows.

Table 2. Frequencies of Spectral Lines Observed in Ionized Solid Hydrogen

Frequencies (in cm^{-1})	Assignments
4149.660 4148.24 4139.54	Shifted H_2 stretching
3970.7 3957.2 3764.6 3756.7	H_2 stretching in H_n^+
3569.6 3519.5 3426.9 3417.2 3317.2	ν_1 of H_3^+ in H_n^+
2230.2 2132.9 2109.7	ν_2 of H_3^+ in H_n^+

Observation of Extremely Narrow Spectrum in SolidH_2

Serendipity

We took spectrum of pure rotational transition J = 6 ← O induced by 2^6-pole (tetrahexacontapole) moment of H_2. This was not in my proposal. I wanted to observe the spectrum simply to test the sensitivity of our spectrometer. I was not surprised by the observation of this novel spectrum itself, but was amazed by the sharpness of the spectrum. Usually solid state spectra are very broad because of strong intermolecular interactions and real high resolution spectroscopy is not needed. This is

the reason why I envisaged using the medium resolution (0.013 cm^{-1}) BOMEM DA-2 spectrometer rather than the highest resolution laser spectrometer. Since we had these latter spectrometers in our laboratory for excited H_3^+ work discussed later, we could study the new spectral line using our state-of-the-art laser spectrometer. We find under certain conditions the solid state lines are much sharper than gaseous lines! This finding opened up a new area of high resolution solid state spectroscopy.

Experiment

In view of the anticipated weakness of the J - 6 ← O line which is highly forbidden in the usual sense, we made a long (10 cm) cell for this work. When the spectrum was observed with good signal-to-noise ratio and the unexpected narrow width, we started to use our high frequency laser spectrometer. The schematic diagram of the apparatus is given in Fig. 4. We use a nonlinear optical crystal ($LiNbO_3$) to take a difference of Ar laser radiation (488 nm) and tunable dye laser radiation (680-550 nm) to generate frequency tunable infrared radiation. We use a KDP crystal (potassium dihydrogen phosphate) optical modulator to generate radio-frequency sidebands on the Ar laser radiation which are transferred due to the optical nonlinearling of $LiIO_3$ to infrared radiation. By switching the rf on and off, we effectively achieve the symmetric frequency modulation which produces a second order derivative line shape. This method picks up sharp spectral lines very effectively.

The Tetrahexacontapole Induced Transition

The observed spectrum of the J = 6 ← O pure rotational transition is shown in Fig. 5. The most amazing thing about this line was that it had a

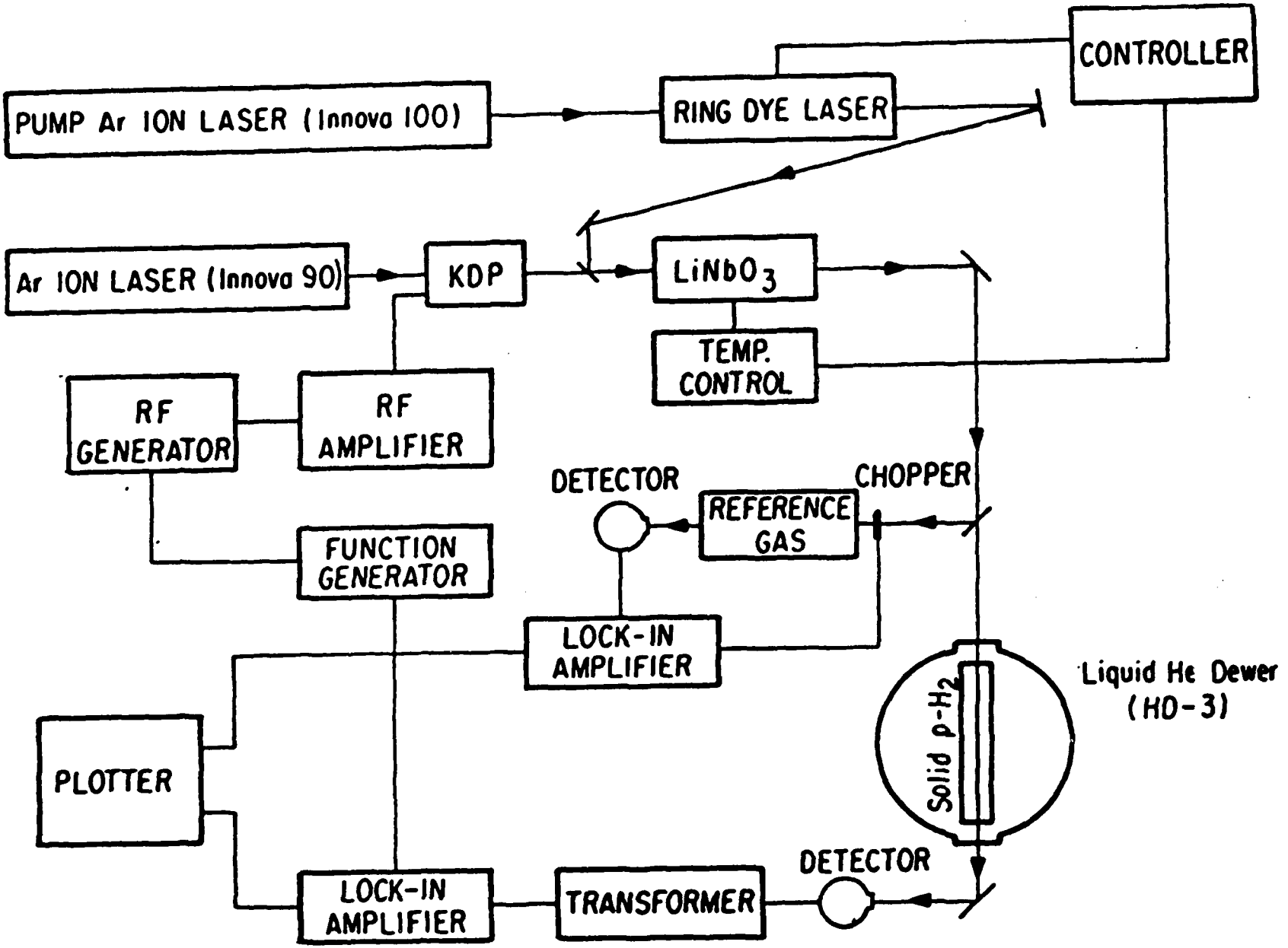


Figure 4. Experimental scheme for the ultrahigh resolution solid hydrogen spectroscopy.

linewidth of ~90 MHz. Other spectral lines of this nature are summarized in Table 3.

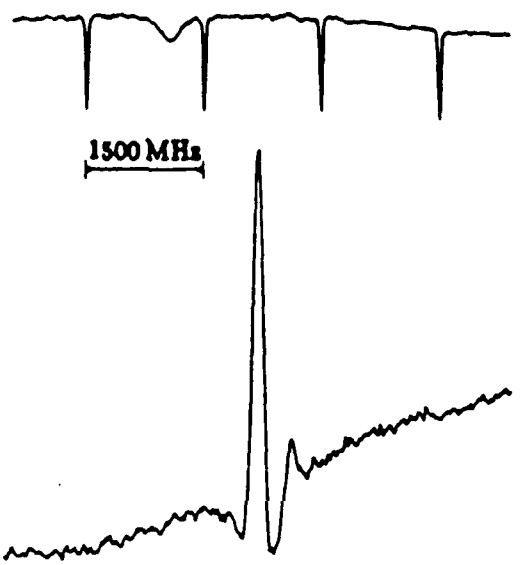


Fig. 5. Difference frequency laser spectrum of the $W_0(0)$ transition in p-H_2 solid by tone-burst modulation at 90 MHz. The peak is at 2410.5384 cm^{-1}, with a width 0.003 cm^{-1} HWHM. The path length is 11.5 cm, T=4K, and the o-H_2 concentration is 0.2%.

Table 3. Observed single and double transitions in solid hydrogen. All results are from this work with FTIR, unless noted. Resolution is 0.04 cm^{-1} for single transtions, 4 cm^{-1} for double transitions.

Single transitions	ν_{obs} (cm^{-1})	ν_{gas}[a] (cm^{-1})	Γ HWHM (cm^{-1})	$\tilde{a}$ ($cm^3 s^{-1}$)	$J=1$ (%)
$S_0(0)$	355.6(1)[b]	354.37	0.1[c]	5.2×10^{-14}	2
$U_0(0)$	1167.10[d]	1168.80	0.125	5.1×10^{-16}	0.2
$W_0(0)$	2410.5384(20)[e]	2414.896	0.003	3.3×10^{-19}	0.2
$Q_{1-0}(1)$	4146.54	4155.255	0.035		0.2
$S_{1-0}(0)$	4485.97[f]	4497.840	0.1	3.3×10^{-15}	2
$U_{1-0}(0)$	5261.28	5271.372	0.10[g]	6.6×10^{-17}	0.2
$W_{1-0}(0)$	6441.81(0.01)	6454.38	0.04[h]	1.1×10^{-19}	0.2

Double transitions	ν_{obs} (cm^{-1})	$J=1$ (%)	Double transitions	ν_{obs} (cm^{-1})	$J=1$ (%)
$U_0(1)+S_0(1)$	1975	50	$U_0(0)+S_{1-0}(1)$	5873	50
$U_0(1)+S_0(0)$	2206	50	$U_{1-0}(1)+S_0(0)$	6039	50
$U_{1-0}(0)+S_0(0)$	5615[i]	0.2	$U_0(1)+S_{1-0}(0)$	6107	50
$U_0(0)+S_{1-0}(0)$	5654[j]	0.2	$U_{1-0}(1)+S_0(1)$	6274	50
$U_{1-0}(0)+S_0(1)$	5848	50	$U_0(1)+S_{1-0}(1)$	6325	50

Vibration-Libration Transitions of J = 1 Impurity H_2

The unexpected sharp spectral line mentioned above immediately suggested to me that perhaps there are enormous numbers of other spectral lines which can be observed very sharply in solid H_2. Recalling the earlier microwave work by Hardy and Berlinsky, I took spectra of J=1 impurity H_2 in mostly concerted solid para (J=1) H_2. Figure 6 shows a portion of the observed spectrum. The intricate structure of the lines is due to the quadrupole-quadrupole interaction between J=1 H_2 placed in a variety of relative positions in the H_2 crystal. The linewidth shown on the upper right insert of the trace is ~10 MHz (HWHM) which is smaller than the typical Doppler broadened gaseous linewidth by a factor of nearly 50! This has opened up the new field of ultrahigh resolution spectroscopy of impurities in solid hydrogen. This will be pursued vigorously in the next term.

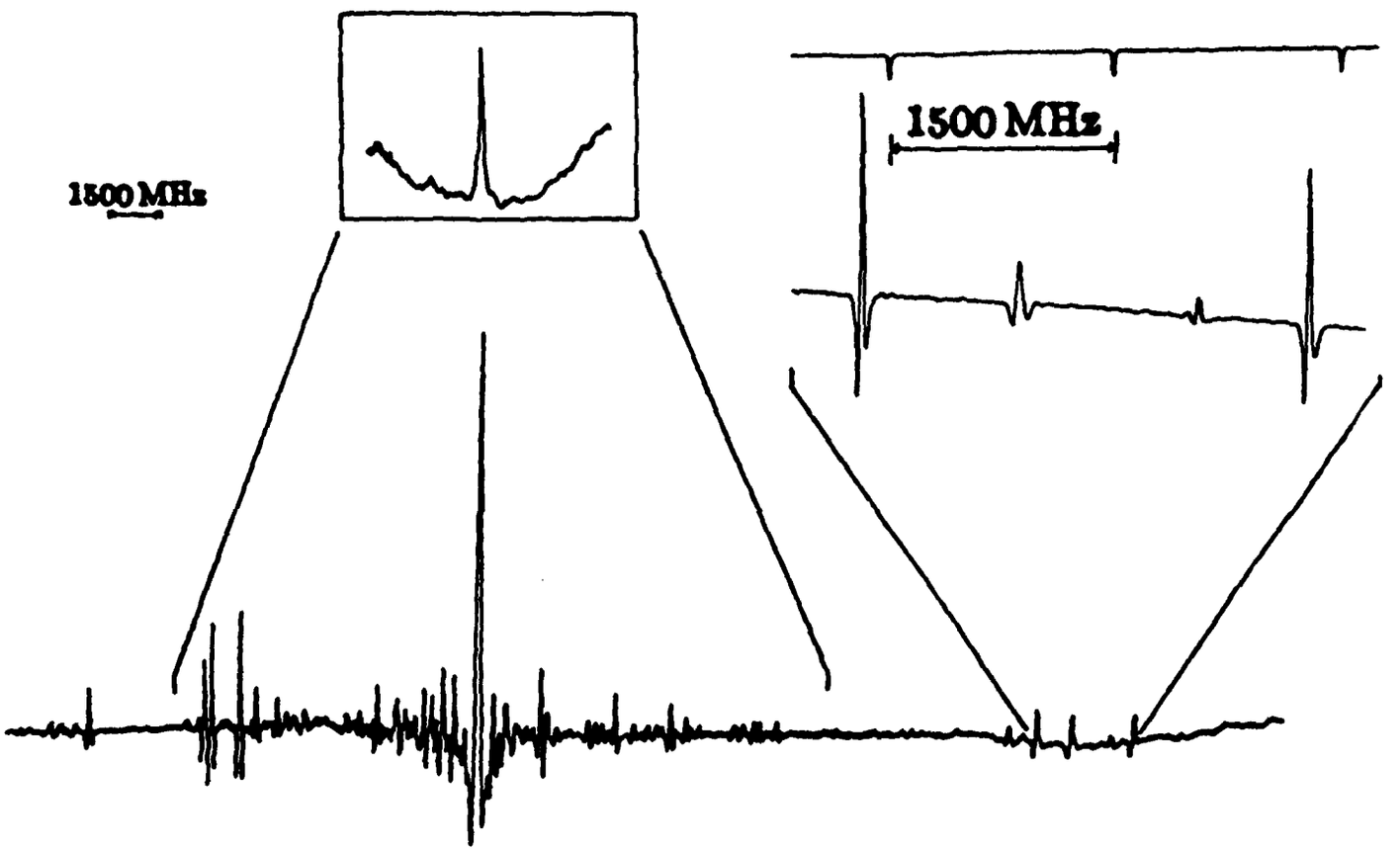


Fig. 6. The $Q_1(1)$ infrared spectrum of the J=1 impurity hydrogen in 99.8% para hydrogen solid. Inset: Chopper modulated laser spectrum. Bottom trace: 90 MHz tone burst spectroscopy revealing intricate structures due to intermolecular interaction between J=1 hydrogen molecules. Top right: A detailed scan of part of the spectrum using tone burst modulation at 20 MHz.

Spectroscopy of Vibrationally Hot Bands of H_3^+

Idea

This study was well conceived and described in my proposal. Our object was to study the excited states $2\nu_2(l = 2)$, $2\nu_2(0)$, and $\nu_1 + \nu_2$, using vibrationally hot and rotationally cool H_2-He plasmas. This has been completed. We have also completed the observation of the overtone band $2\nu_2(l = 2) \leftarrow 0$ which was not anticipated in the proposal. There was a totally unexpected development, the discovery of H_3^+ emission spectrum in Jupiter which is discussed later.

Experiment

In order to observe the hot bands and the overtone band of H_3^+, we had to extend the frequency coverage of our difference-frequency spectrometer. This has been achieved by introducing $LiIO_3$ crystal as the nonlinear element and angle tuning for phase matching. This grant supported construction of this part of the apparatus. The crucial part of the optical arrangement is shown in Fig. 7.

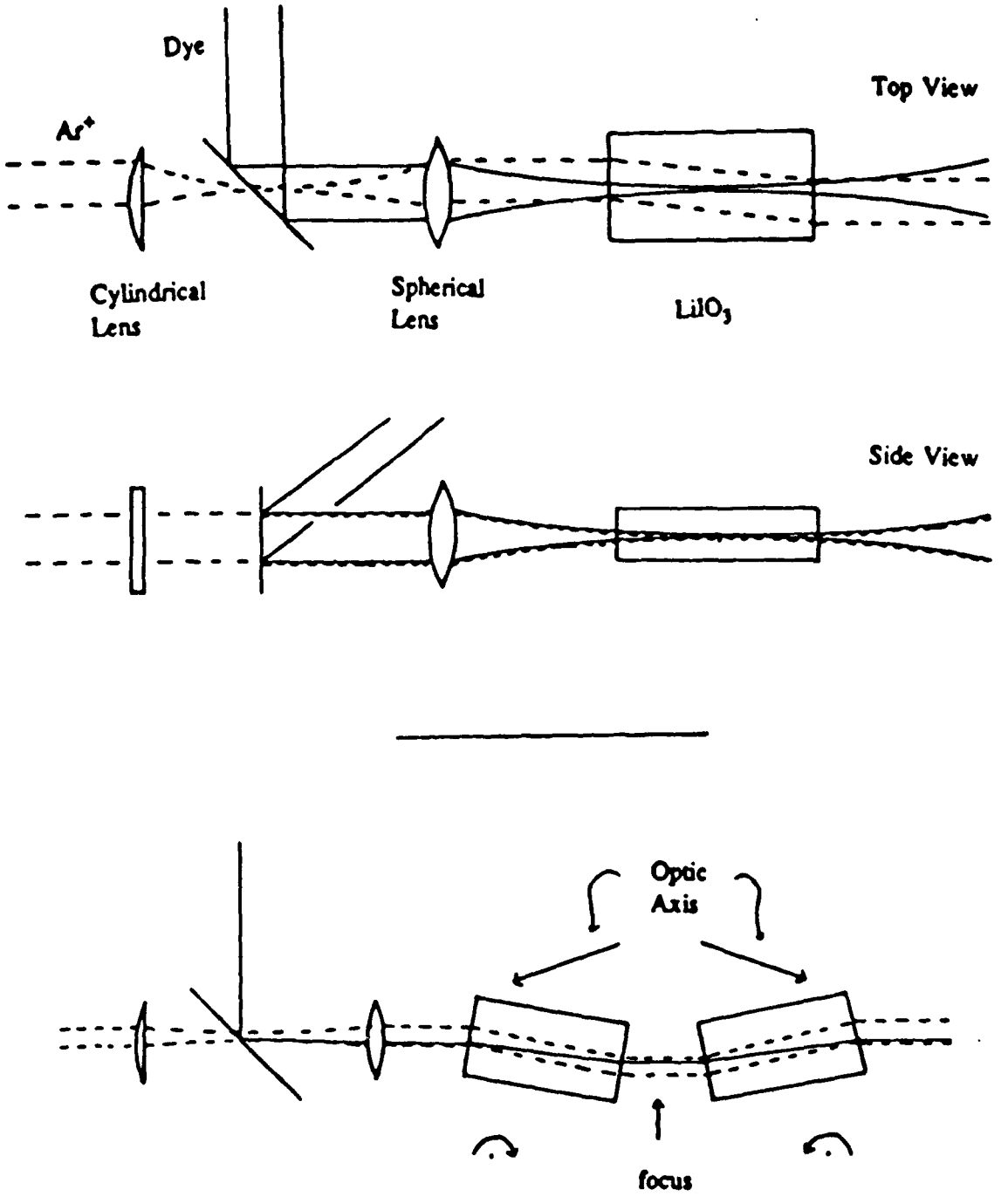


Fig. 7. The $LiIO_3$ non-linear optical device.

This device allowed us to cover a wide frequency range of 5000 cm^{-1} ~ 1800 cm^{-1}, albeit with lower power and thus lower sensitivity.

The production of H_3^+ with high vibrational temperature but with low rotational temperature was possible using a special discharge tube nicknamed "black widow". A picture of this liquid nitrogen-cooled discharge tube is shown in Fig. 8.

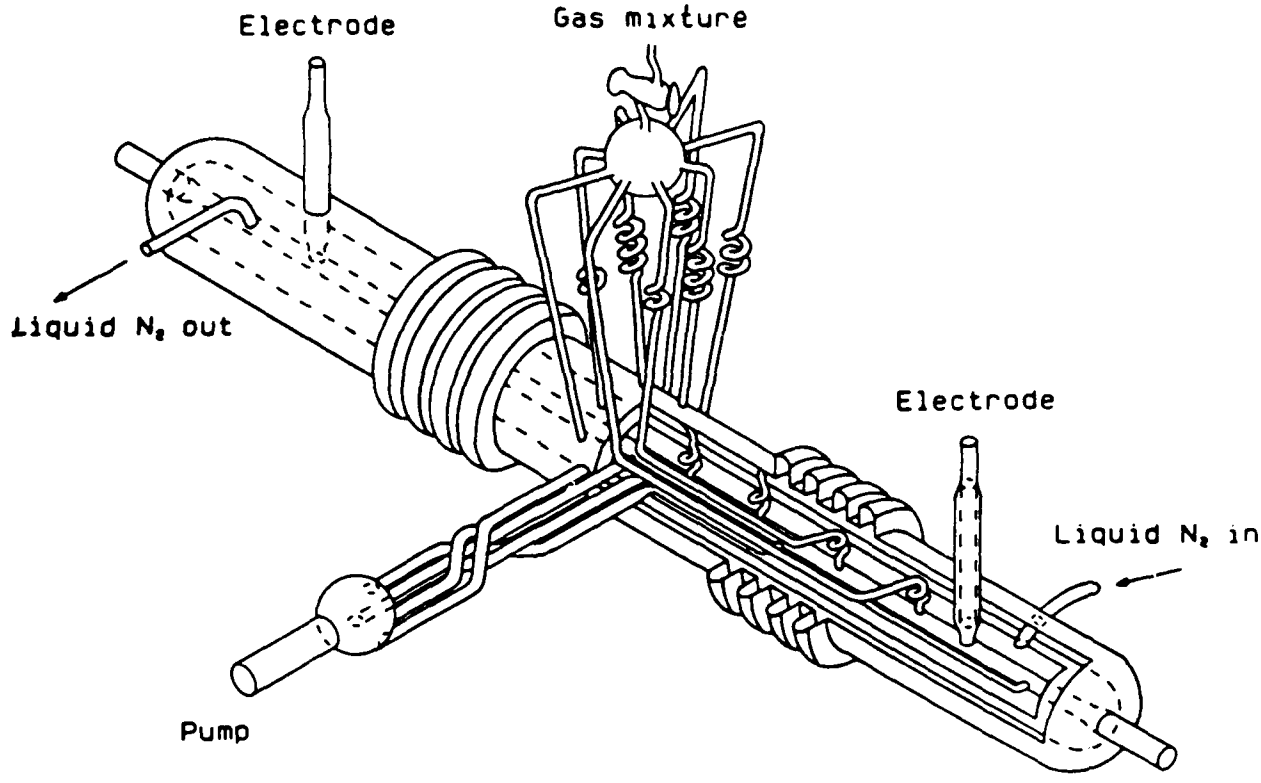


Fig. 8. The multiple inlet-outlet liquid nitrogen cooled plasma tube (nicknamed "Black Widow").

The observed high vibrational temperature (≥ 1000 K) and the low rotational temperature (~250 K) are due to the high ionization potential of He (24.6 eV) and liquid N_2 cooling, respectively. While He is the dominating discharge gas, it does not steal the proton from H_3^+ because of its very low proton affinity (1.9 eV).

Hot Bands

An energy level diagram indicating various H_3^+ excited states is shown in Fig. 9.

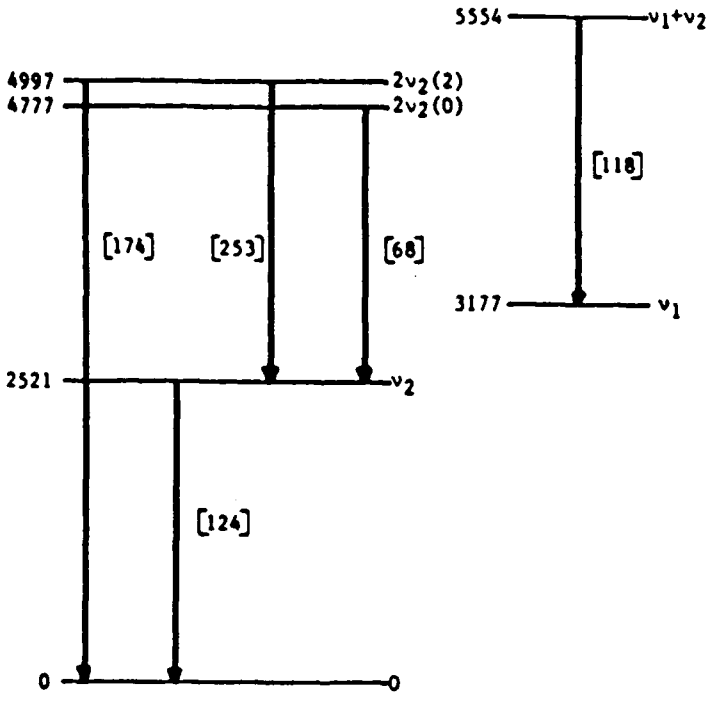


Fig. 9. The vibrational energy levels of H_3^+.

We have observed 66 transitions belonging to the $2\nu_2(2) \leftarrow \nu_2$ band, 14 transitions belonging to the $2\nu_2(0) \leftarrow \nu_2$ band, and 21 transitions belonging

to the $\nu_1+\nu_2 \leftarrow \nu_1$ band. During these extensive studies we have assigned 13 new lines belonging to the fundamental $\nu_2 \leftarrow 0$ band. Tables 5 and 6 list some of the observed transitions. As we go to higher vibrationally excited states, the energy level patterns get more chaotic due to higher vibration-rotation interaction, and the usual spectroscopic theory does not explain the observed frequencies. It was extremely lucky that Steven Miller and Jonathan Tennyson have recently done theoretical calculations using a supercomputer and have sent us the results prior to publication. Our characterization of the spectrum is very much based on their calculation.

Overtone Bands

The successful extension of the frequency coverage of our spectrometer has enabled us to observe the overtone band $2\nu_2(2) \leftarrow 0$ with the band origin of ~ 5000 cm^{-1}. Figure 10 is a computer-generated stick diagram of the overtone band.

TABLE 5. Observed and assigned transitions in the $2\nu_2, l=2 \leftarrow \nu_2$ band of H_3^+ (in cm^{-1})[a]

J_u	G_u	U_u	←	J_l	G_l	U_l	ν_{obs}	ν_{calc}
3	5	2		4	5	1	2241.3466	2241.5
3	1	-2		3	1	1	2422.9831	2422.2
4	1	-2		4	1	1	2423.6751	2422.8
4	0	-2		4	0	1	2449.7949	2449.6
0	2	2		1	2	1	2449.8849	
4	2	-2		4	2	-1	2456.2727	2455.7
2	0	-2		2	0	1	2474.0543	2473.4
3	1	-2		3	1	-1	2483.5530	2482.8
4	1	2		4	1	1	2508.7571	2508.1
3	1	2		3	1	1	2510.2912	2509.6
2	1	2		2	1	1	2514.6191	2514.1
1	1	2		1	1	1	2515.7548	2515.2
4	1	-2		4	1	-1	2520.6767	2519.8
4	2	2		4	2	1	2536.9314	2536.4
1	2	2		1	2	1	2539.4509	2539.0
3	2	2		3	2	1	2541.2928	2540.7
3	0	2		3	0	-1	2541.4326	2540.6
2	2	2		2	2	1	2542.4670	2542.1
3	3	2		3	3	1	2554.2758	2553.9
2	3	2		2	3	1	2566.9039	2566.6
3	1	2		3	1	-1	2570.8584	2570.2
4	3	2		4	3	1	2577.6294	2577.1
3	4	2		3	4	1	2579.7483	2579.6
4	4	2		4	4	1	2583.1533	2583.1
4	5	2		4	5	1	2596.5199	2596.6
3	2	2		3	2	-1	2602.3666	2601.8
1	1	2		0	1	1	2603.8831	
4	1	2		4	1	-1	2605.7634	2605.1
4	2	2		4	2	-1	2628.0974	2627.5
4	3	2		4	3	-1	2665.7293	2665.2
2	0	-2		1	0	-1	2670.2342	2669.5
2	1	2		1	1	1	2695.4196	2694.9
3	1	-2		2	1	1	2696.1102	2695.4
2	2	2		1	2	1	2718.2616	2718.0
4	2	-2		3	2	1	2724.0581	2723.5
3	1	-2		2	1	-1	2730.8869	2730.1
3	0	2		2	0	1	2754.5347	2753.8
4	1	-2		3	1	1	2783.3247	2782.4
3	1	2		2	1	1	2783.4170	2782.8
4	2	-2		3	2	-1	2785.1212	2784.6
3	2	2		2	2	1	2809.7667	2809.2
3	3	2		2	3	1	2816.8426	2816.5
3	1	2		2	1	-1	2818.1960	2817.5
4	1	2		3	1	1	2868.4035	2867.8
4	0	-2		3	0	-1	2870.8895	2870.0
4	2	2		3	2	1	2895.8735	2895.3
4	4	2		3	4	1	2932.9879	2932.8
4	3	2		3	3	1	2934.1551	2933.6

TABLE 6. Observed and assigned transitions in the $\nu_1 + \nu_2 \leftarrow \nu_1$ band of H_3^+ (in cm^{-1})[a]

J_u	G_u	U_u	←	J_l	K_l	ν_{obs}	ν_{calc}
3	3	1		4	3	2089.3052*	2089.4
3	4	1		4	4	2097.7451	2098.4
1	2	1		2	2	2241.0773	2240.9
3	3	1		3	3	2424.7965*	2424.8
4	3	1		4	3	2433.9009*	2433.8
4	4	1		4	4	2438.5087	2438.8
2	0	1		1	0	2572.2203	2571.6
3	2	-1		2	2	2606.2958	2606.3
3	1	1		2	1	2671.1417	2670.7
3	2	1		2	2	2672.7991	2672.5
4	3	-1		3	3	2672.9580*	2672.9
4	2	-1		3	2	2680.6312	2680.7
4	3	1		3	3	2769.3931	2769.2

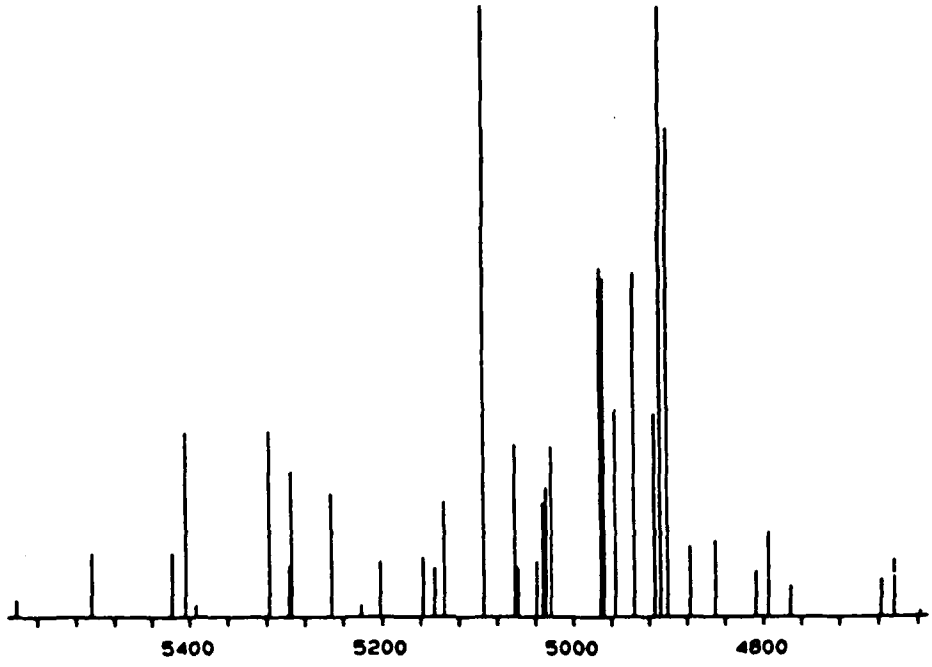


Fig. 10. Computer generated stick diagram of the observed H_3^+ overtone band.

We have observed and assigned 33 lines belonging to the overtone band. This band has the unusual selection rule of $\Delta|K-l|=3$ contrary to the usual $\Delta|K-l|=0$. This has allowed us to determine the absolute energy levels of H_3^+ in the ground state and in the ν_2, $2\nu_2(2)$, and $2\nu_2(0)$ states. It also provides atronomers with accurate line positions and relative intensities which they can use to study various astronomical objects.

H_3^+ Emission Spectrum in Jupiter

Serendipity

The H_3^+ ion is one of the most fundamental hydrogen species, and its presence in space has been predicted by many theorists for the last several years.. I had been searching for this species in molecular clouds in interstellar space, but I had never dreamt of searching for it in planetary atmospheres. While we were studying the highly excited states of H_3^+ in the laboratory, the French astronomers Maillard and Drossart observed strong infrared emission lines in Jupiter. Using our laboratory data, Jim Watson at the Herzberg Institute of Astrophysics was able to assign the spectrum to the H_3^+ $2\nu_2 \rightarrow 0$ overtone emission band. This discovery was made purely by chance; Maillard and Drossart were studying H_2 emission in Jupiter and *accidentally hit upon the* H_3^+ *spectrum. I felt really stupid* not to have thought about Jupiter!

Observation of the Fundamental Band

The news of the astronomical observation of H_3^+ excited me to no measure. I decided to drop all my scheduled activity this summer and observe Jupiter myself. (I was scheduled to attend two international conferences in China.) Tom Geballe and I observed beautiful emission lines of the fundamental band of H_3^+. Two examples are shown in Figs. 11 and 12.

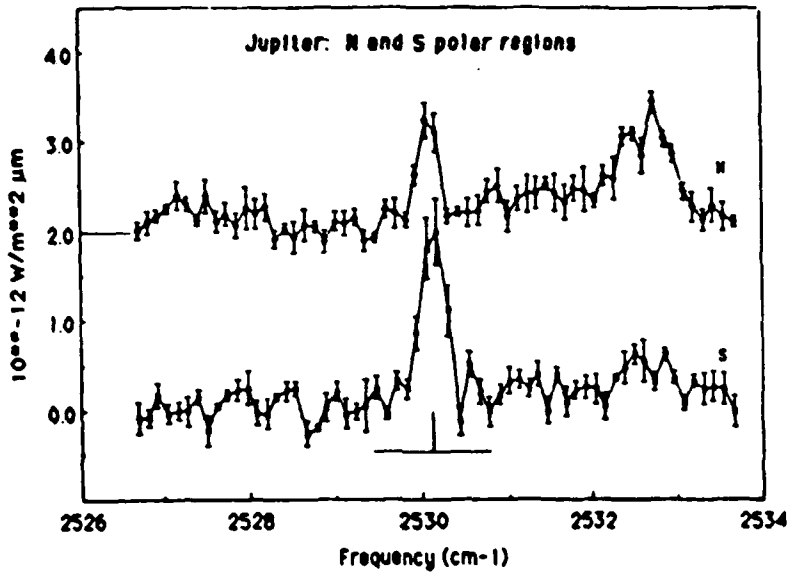


Fig. 11. Spectra of the 1,0,-1 → 1,0 line of H_3^+ at 2530 cm^{-1} in the polar regions of Jupiter, observed at longitudes of 160° and 181°.

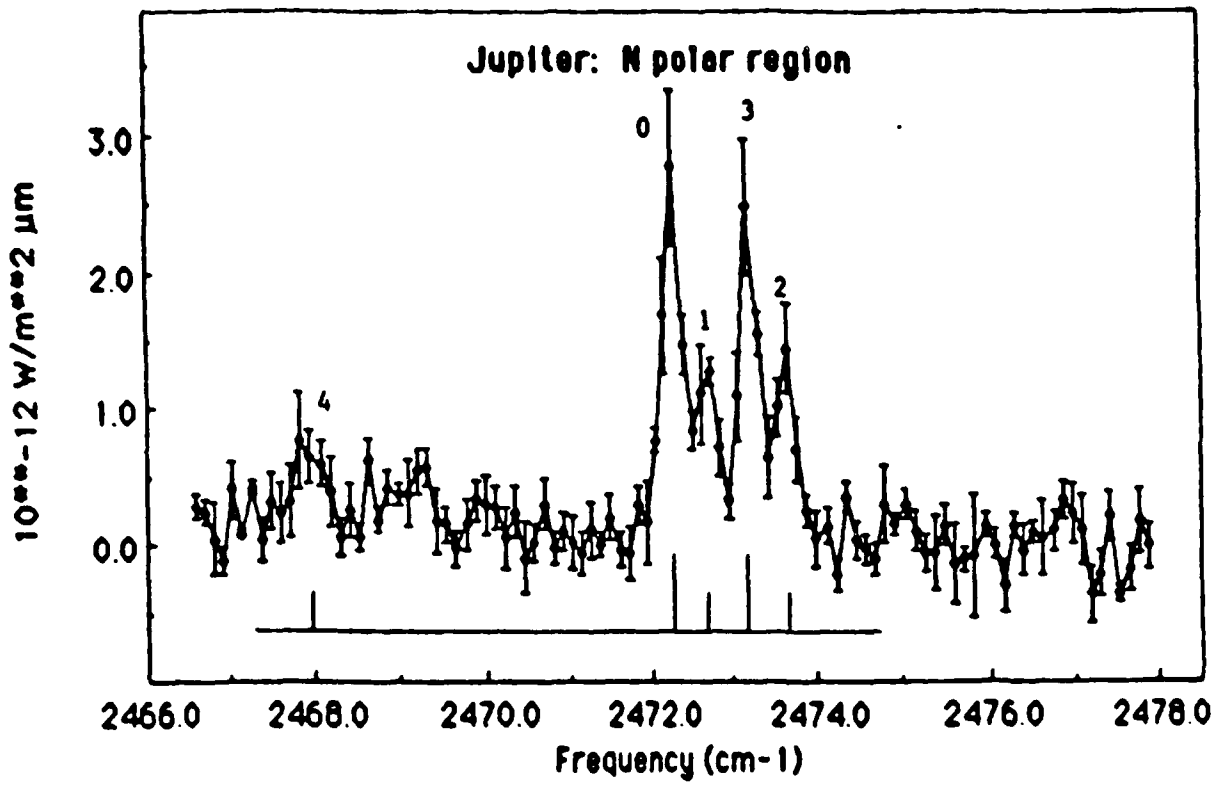


Figure 12. A quartet of lines in Jupiter connecting J=5 levels in the ν_2 band of H_3^+. See Table 1 for identifications. The weak feature at 2468 cm^{-1} may be a blend of an H_3^+ line with H I Br α.

Acknowledgement

These have been an extremely productive three years, and I am very grateful to the Astronautics Laboratory (AFSC) for supporting our research.

PERSONNEL FOR EACH PROJECT

II, III	Mitchio Okumura	Postdoctoral Fellow, now an Assistant Professor at California Inst. of Technology
	Man-Chor Chan	Graduate Student
	Brent Rehfuss	Graduate Student, now a post-doctorate fellow at Ohio State University
	Li-Wei Xu	Graduate Student
	Charles Gabrys	Graduate Student
	Stephen Lee	Graduate Student
IV	Moungi Bawendi	Graduate Student, now an Assistant Professor at MIT
	Brent Rehfuss	Graduate Student, now a postdoctorate fellow at Ohio State University
	Li-Wei Xu	Graduate Student
	Charles Gabrys	Graduate Student
V	Tom Geballe	Astronomer at UKIRT

PUBLICATIONS

II. "Infrared Spectrum of Ionized Solid Hydrogen", M.C. Chan, M. Okumura and T. Oka. Manuscript in preparation.

III. "High Resolution Infrared Spectroscopy of Solid Hydrogen. The Tetrahexacontapole-induced $\Delta J=6$ Transitions", M. Okumura, M.C. Chan and T. Oka, Phys. Rev. Lett. 62, 32 (1989).

"Observation of Very Narrow Transitions in the Infrared Spectrum of Solid Hydrogen", M.C. Chan, M. Okumura, B.D. Rehfuss, L.W. Xu, and T. Oka. Manuscript in preparation.

IV. "Observation of Vibrational Hot Bands of H_3^+", M. Bawendi, B.D. Rehfuss and T. Oka. J. Chem. Phys., submitted.

"Observation of Overtone Band of H_3^+", L.W. Xu, C. Gabrys, and T. Oka, J. Chem. Phys., submitted.

V. "Observation of the 4 μm Fundamental Band of H_3^+ in JUPITER", T. Oka and T.R. Geballe, Astrophys. J. 351, L53 (1990).